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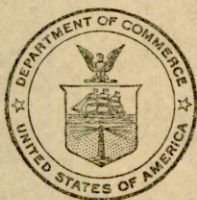
HIGH FIRE PORCELAIN GLAZES

BY

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HIGH FIRE PORCELAIN GLAZES

By H. H. Sortwell

A great deal of material has been published on porcelains of all types, but systematic information on porcelain glazes fired at the higher temperatures is more limited.

Stull¹ thoroughly covered the field for glazes maturing at cone 11. Stull and Howat² investigated the field at cone 9 and reported deformation temperature studies for the glazes made.

Since no detailed information was to be had on glazes of this type for high fire porcelain, chemical porcelain, spark plugs, pyrometer tubes, etc., maturing from cones 12 to 16, the following investigation was undertaken.

Compositions Studied.—As originally laid out the field consisted of 35 members with 3, 4, 5, 7, 9, 11, and 13 equivalents of silica, and alumina corresponding to alumina-silica ratios of 1:10, 1:8, 1:6, 1:5, and 1:4. The RO members were constant at 0.7 C₂O and 0.3 K₂O. This covered the field with fair uniformity when plotted both by the empirical formula method and by batch weights. Later, to round out the deformation temperature study, 15 additional glazes were made with silica 4, 5, 7, 9, 11, and 13 equivalents with the alumina-silica ratio of 1:12; silica 5, 7, 9, 11, and 13 equivalents with the alumina-silica ratio of 1:15; and silica 7, 9, 11, and 13 equivalents with the alumina-silica ratio of 1:20.

Procedure.—The glazes were weighed out separately in 1 kg batches and ground three hours in small ball mills. The materials used were analyzed and the results given in Table 1.

A small quantity of each glaze was evaporated to dryness and molded into test cones for the deformation temperature determinations, which were made in a small gas furnace. The temperature was raised to 1100° C in one hour and from 1100° C on at the rate of 50° per hour. The temperature measurements were made with a platinum-rhodium thermocouple and a Leeds-Northrup potentiometer indicator. Five cones were tested at a time, the thermo-

¹ Trans. Amer. Cer. Soc., 14, pp. 62-70.

² Trans. Amer. Cer. Soc., 16, pp. 454-460.

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couple junction being within three-eighths inch of each cone. Uniform temperatures were maintained within the furnace as shown by Orton cones. Two or more determinations were made on each glaze, checks within 5° C being obtained.

TABLE 1.—Results of Analyses of the Material Used

Components	Flint	North Carolina kaolin	Maine feldspar	Whiting
SiO ₂	98.43	41.96	72.85	0.91
Fe ₂ O ₃26	.52	.48	.30
Al ₂ O ₃80	35.95	15.45	.34
CaO.....		.24	.31	55.02
K ₂ O.....			7.89	
Na ₂ O.....			2.31	
MgO.....				.44
Loss on ignition.....	.14	20.40	.25	43.44
Total.....	99.63	99.07	99.54	100.45

The glazes were applied by dipping on porcelain cups 2½ inches in diameter, 2½ inches deep, and one-eighth inch thick, which had previously been biscuited to cone 08 in a slow oxidizing fire. The composition of the body used was as follows:

North Carolina kaolin.....	31
Florida kaolin.....	12
Tennessee ball clay No. 5.....	5
Flint.....	34
Feldspar.....	18

Four glaze burns were made in a gas-fired kiln, to cone 10 in 20 hours, to cone 12 in 20 hours, to cone 14 in 22 hours, and to cone 16 in 24 hours. Reducing conditions were maintained up to cone 8, but from that point on reduction was diminished until the fire was neutral or slightly oxidizing at the finish.

Deformation Temperatures.—The silica and alumina equivalents of all the glazes and their deformation temperatures are given in Table 2. The deformation eutectic axis in the part of the field previously covered practically agrees with the work of Stull and Howat. The softening temperatures found in the present work are lower, as would be expected, due to the slower rate of heating. Since the field was not covered as closely in this work, the slight variations are not shown.

TABLE 2

No.	Al ₂ O ₃	SiO ₂	Al ₂ O ₃ : SiO ₂	Deforma- tion tempera- ture, °C.	No.	Al ₂ O ₃	SiO ₂	Al ₂ O ₃ : SiO ₂	Deforma- tion tempera- ture, °C.
1	0.300	3.0	1:10	1173	26	1.100	11.0	1:10	1275
2	.375	3.0	1:8	1146	27	1.375	11.0	1:8	1278
3	.500	3.0	1:6	1109	28	1.833	11.0	1:6	1300
4	.600	3.0	1:5	1109	29	2.200	11.0	1:5	1350
5	.750	3.0	1:4	1134	30	2.750	11.0	1:4	1418
6	.400	4.0	1:10	1137	31	1.300	13.0	1:10	1315
7	.500	4.0	1:8	1115	32	1.625	13.0	1:8	1317
8	.666	4.0	1:6	1114	33	2.166	13.0	1:6	1336
9	.800	4.0	1:5	1124	34	2.600	13.0	1:5	1386
10	1.000	4.0	1:4	1210	35	3.250	13.0	1:4	1461
11	.500	5.0	1:10	1124	A ₁	.333	4.0	1:12	1175
12	.625	5.0	1:8	1124	A ₂	.416	5.0	1:12	1151
13	.833	5.0	1:6	1157	A ₃	.583	7.0	1:12	1148
14	1.000	5.0	1:5	1173	A ₄	.750	9.0	1:12	1183
15	1.250	5.0	1:4	1223	A ₅	.916	11.0	1:12	1252
16	.700	7.0	1:10	1147	A ₆	1.083	13.0	1:12	1317
17	.875	7.0	1:8	1159	B ₁	.333	5.0	1:15	1169
18	1.166	7.0	1:6	1208	B ₂	.466	7.0	1:15	1149
19	1.400	7.0	1:5	1218	B ₃	.600	9.0	1:15	1180
20	1.750	7.0	1:4	1292	B ₄	.733	11.0	1:15	1230
21	.900	9.0	1:10	1209	B ₅	.867	13.0	1:15	1376
22	1.125	9.0	1:8	1224	C ₁	.350	7.0	1:20	1207
23	1.500	9.0	1:6	1230	C ₂	.450	9.0	1:20	1237
24	1.800	9.0	1:5	1248	C ₃	.550	11.0	1:20	1398
25	2.250	9.0	1:4	1370	C ₄	.650	13.0	1:20	1410

The results are plotted for the molecular variations of alumina and silica (Fig. 1) and for the batch weights (Fig. 2), for which

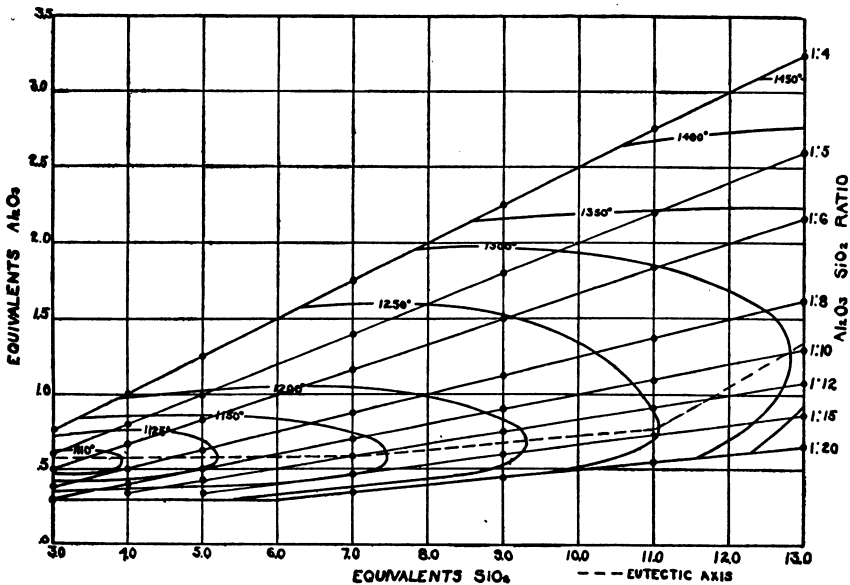


FIG. 1.—Deformation temperatures

the glazes were calculated into percentages of clay, flint, and fluxes (feldspar and whiting in the proportion of 167 feldspar to 70 whiting).

As shown in Fig. 1, increase in silica to 11 equivalents maintaining the alumina constant has little effect in comparison with alumina in increasing the deformation temperature as the isotherms run in the general direction of the alumina ordinate up to 11 equivalents. Beyond this figure increase in silica has a more pronounced effect on the deformation temperature.

Starting with 0.3 Al_2O_3 and any silica content, increasing the Al_2O_3 lowers the deformation temperature until the eutectic axis is crossed. Further increase in Al_2O_3 raises the deformation temperature.

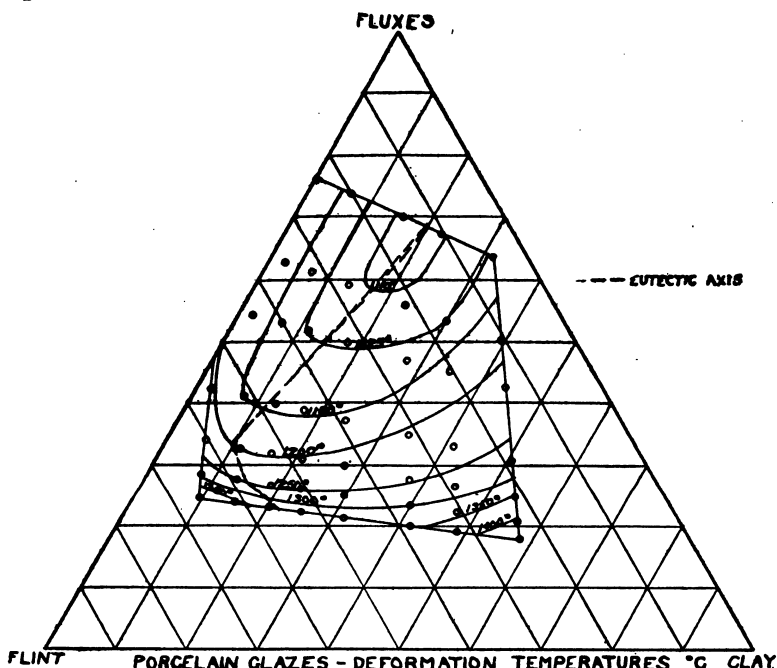


FIG. 2.—Deformation temperatures

The deformation eutectic axis lies at a slight inclination to the ordinate. As the silica content approaches 7 equivalents this inclination rises, and at 11 equivalents it increases much more.

Examination of Fig. 2 shows that increasing flint does not greatly increase the deformation temperature until the composition approaches 60 per cent flint. Further increase in flint increases the temperature rapidly.

Starting with zero clay, additions of clay first lower the deformation temperature, after which further increments of clay increase the temperature gradually until 45 per cent clay is ap-

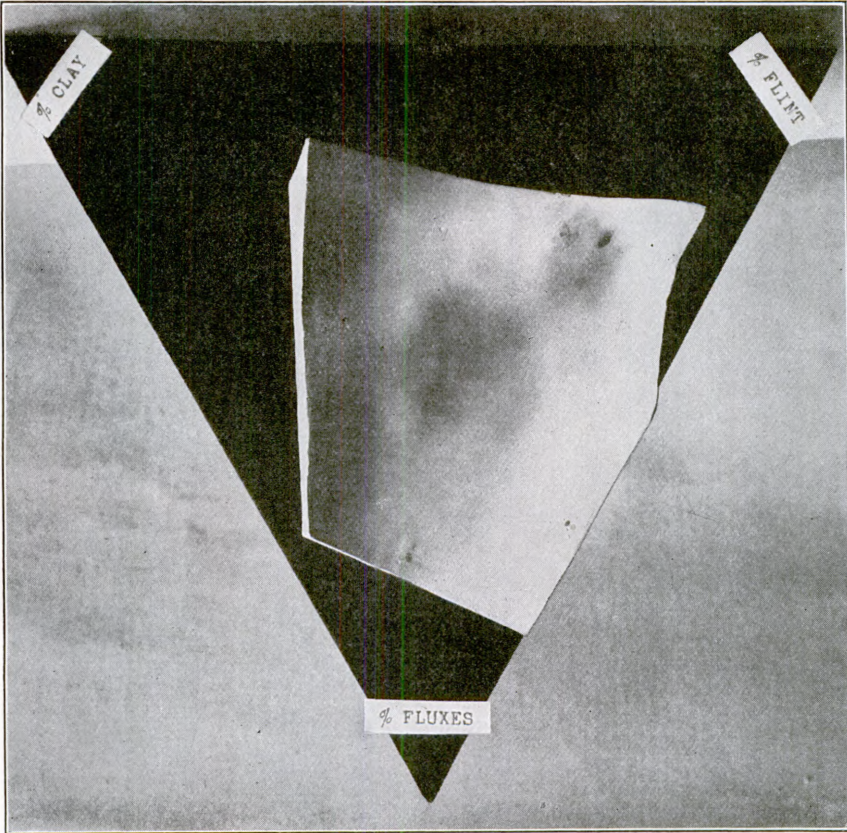
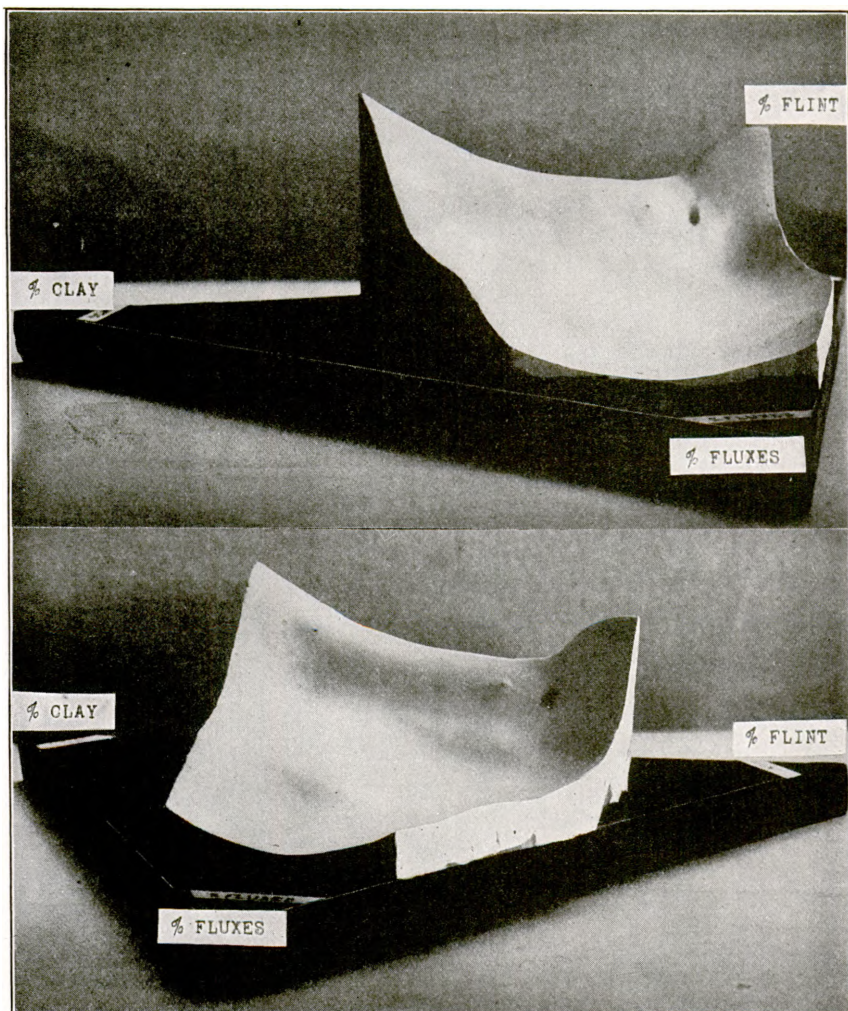


FIG. 3.—Solid diagram of deformation temperatures



FIGS. 4 AND 5.—Solid diagrams of deformation temperatures

proached. From that point the temperature increase with increments of clay is more abrupt.

Decrease in the flux content (feldspar and whiting) increases the temperature of deformation gradually until it approaches 30 per cent, after which further reductions cause a rapid rise in temperature.

The deformation eutectic axis starts at approximately 20 per cent clay, 10 per cent flint, and 70 per cent fluxes, and runs in a straight line to approximately 10 per cent clay, 55 per cent flint, and 35 per cent fluxes. At this point the axis deflects to a higher clay content.

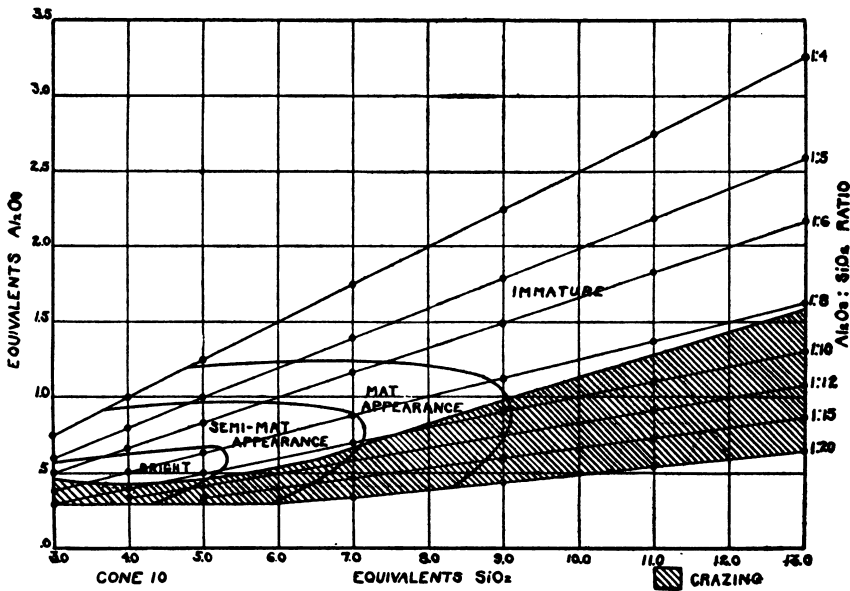


FIG. 6.—Porcelain glazes at cone 10

A plaster of Paris solid diagram was made of the field as plotted in Fig. 2 and is shown in Figs. 3, 4, and 5. This shows plainly within what wide limits the more fusible glazes fall.

Cone 10 Burn.—In Figs. 6 and 7 are shown the results of the cone 10 burn. At this heat treatment only a small part of the field is bright and the craze area comparatively large.

It will be noted that there is a belt surrounding the bright area in which the glazes are of semimat appearance, and surrounding this are glazes of mat appearance. The latter have the characteristic mat texture due to high alumina, while for the high silica glazes the term mat appearance is used only as a criterion of

maturity. Outside of the mat area the glazes are dry and immature.

Fig. 6 shows that the obvious way to correct crazing in this type of glaze is to increase the alumina content by addition of clay.

Cone 12 Burn.—At cone 12, Figs. 8 and 9, the area of good bright glazes has increased and the crazing area receded as would be expected. Glazes 2, 3, and 4 show signs of overburning, as

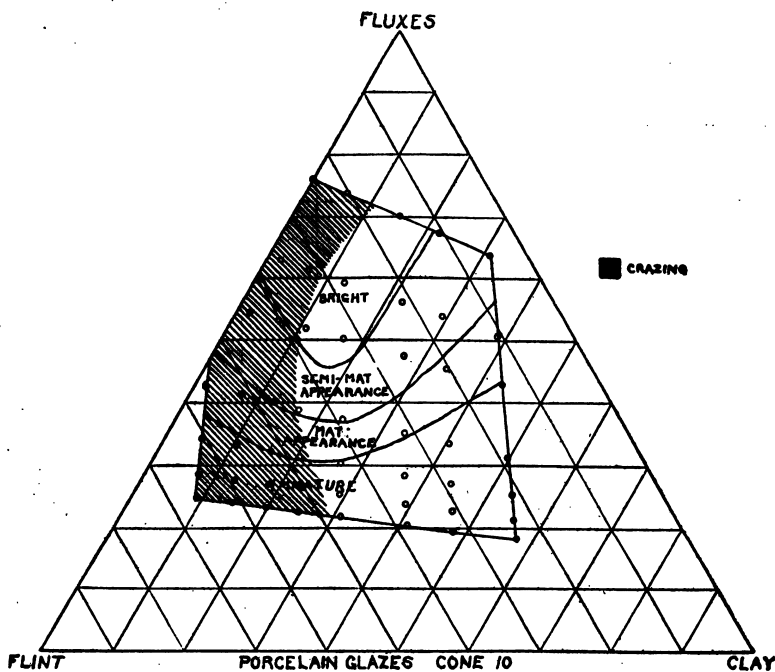


FIG. 7.—Porcelain glazes at cone 10

evidenced by the formation of bubbles which were not present at cone 10. The semimat and mat areas have shifted position in accordance with the change in the area of bright glazes.

Glazes C_1 , C_2 , C_3 , C_4 , B_3 , B_4 , and B_5 , which are the high silica glazes of lowest alumina content and the only glazes of 55 per cent or more flint, show signs of segregation at this fire. This evidenced itself by lines on the surface of the glaze similar to watermarks, but rising from the surface instead of being depressions. It appeared as if the fluxes were drawn to the inside of the glaze, leaving a skeleton of flint at the surface. With the contraction of the body in burning, these high flint glazes did not follow, and consequently had to rise from the surface of the body.

Cone 14 Burn.—Figs. 10 and 11 show that at cone 14 the area of bright glazes and the area of overburned glazes has increased, the craze area receded still further, and the semimat and mat area shifted again.

The softer of the overburned glazes at this temperature were full of bubbles and had run to the bottom of the piece badly.

It was interesting to note that glazes 2 and 3, which were badly overburned and were far out of the craze area at this heat treatment, were crazed. No. 3 had been sound at cones 10 and 12. This seems to be evidence that when this type of glaze is over-

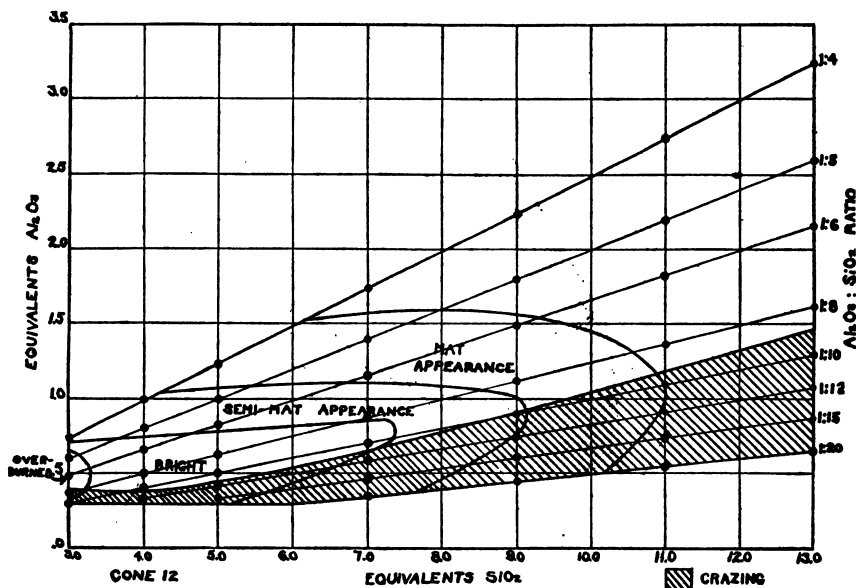


FIG. 8.—Porcelain glazes at cone 12

burned sufficiently, its composition or its physical state is changed enough to cause crazing.

The seven glazes containing 55 per cent or more flint showed segregation as at cone 12.

Cone 16 Burn.—At cone 16, Figs. 12 and 13, the area of bright glazes crosses the entire field, the area of overburned glazes is enlarged and the crazing area smaller. The semimat and mat areas have shifted in accordance with the change in the bright area.

The glazes which were overburned at cone 14 were not included in the cone 16 burn, so that further observation of the effect of

overburning on crazing was not available, as none of the glazes which were overburned at cone 16 but matured at cone 14 had been overburned as much as glazes 2 and 3 at cone 14. The segregation is present in the same glazes at cone 16 as at cone 14.

It is to be noted that although a great many of these mat glazes are such due to immaturity as may be seen by following the charts through the successive burns, those mats and semimats in which the alumina: silica ratio is as high as 1:4 for 3-6 equivalents of silica and as low as 1:6 at 10 equivalents of silica (see

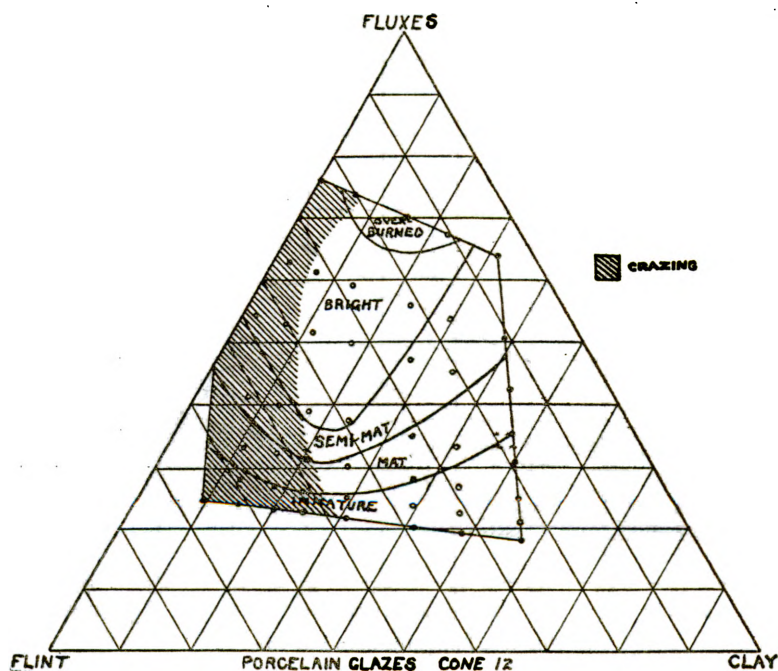


FIG. 9.—Porcelain glazes at cone 12

Fig. 12) are not mats of immaturity. Glazes 5, 10, and 15, which have lower deformation points than most of the bright glazes at cone 16, are still semimats. Glaze No. 5, with a deformation temperature of 1134°C , is still a semimat at cone 16.

In Fig. 12 the high gloss axis and the deformation eutectic axis are plotted for comparison. Except in the vicinity of 0.3 equivalents silica, the best glazes of a given silica content are higher in alumina and a trifle harder than the most fusible glaze of that silica content. The eutectic axis lies partially in the craze area.

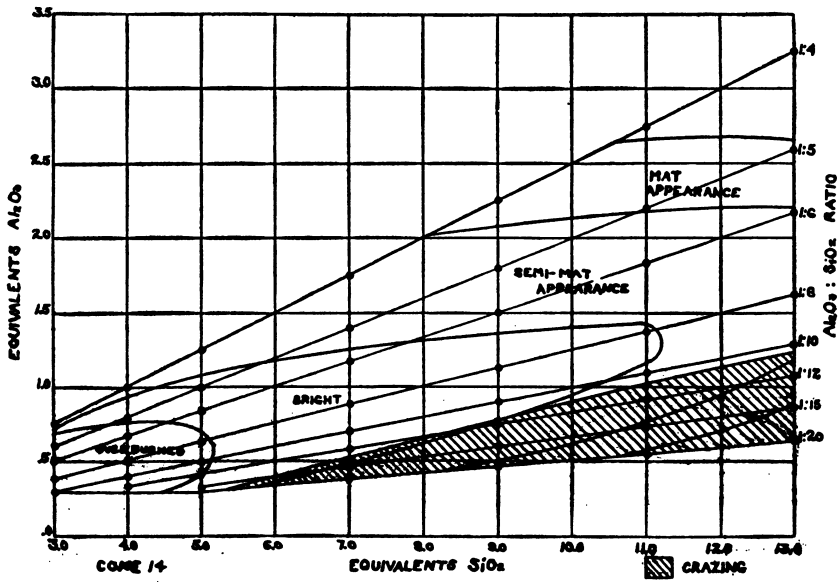


FIG. 10.—Porcelain glazes at cone 14

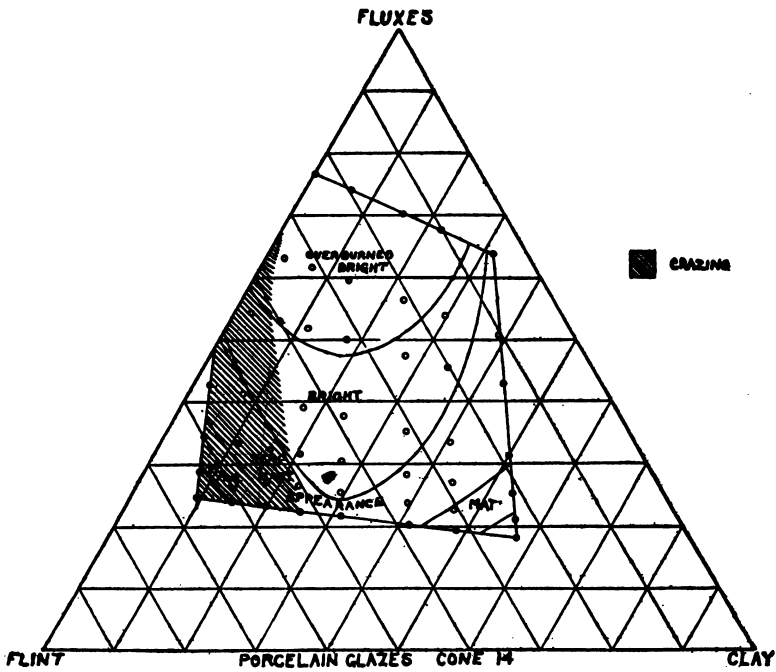


FIG. 11.—Porcelain glazes at cone 14

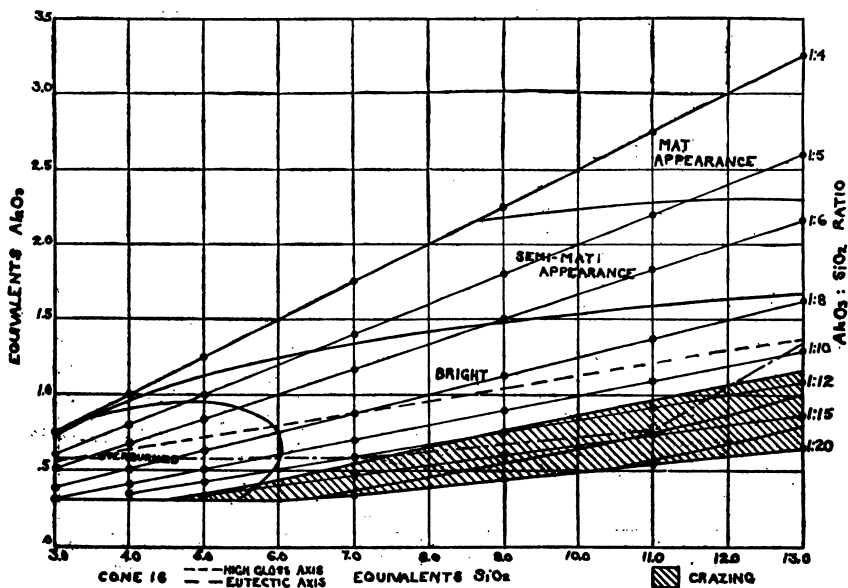


FIG. 12.—Porcelain glazes at cone 16

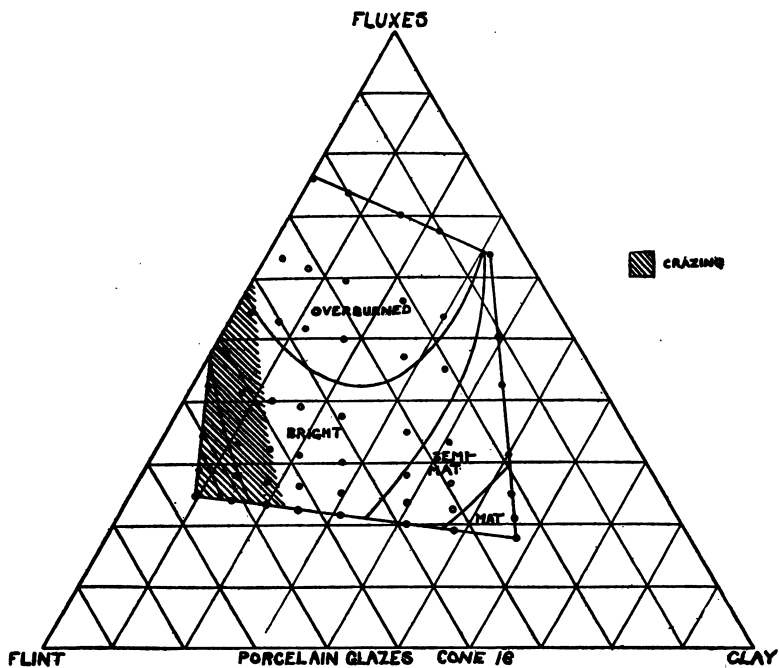
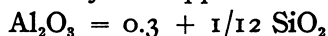


FIG. 13.—Porcelain glazes at cone 16

CONCLUSIONS

There is a wide range of commercially acceptable bright glazes of this type maturing from cones 12 to 16 having a temperature range of from four to five cones.

The best glazes lie along a high gloss axis which is practically a straight line represented by the approximate formula



The range in silica content for a given temperature is wide and becomes greater as the maturing temperature is raised, the possible variations being between 3 to 13 equivalents of SiO_2 . The range in alumina content for a given temperature is very much narrower than the range in silica content.

There is a deformation eutectic axis for this series which lies below the high gloss axis and partially in the crazing area.

The best bright glazes for each heat treatment are found at the center of the area of mature good glazes on the chart.

Mat glazes of this type in which the alumina is high enough to give an alumina: silica ratio of 1:4 for 3 to 6 equivalents of silica and tapering down to 1:6 for 10 equivalents silica are aluminous mats and not mats of immaturity since increasing heat treatment will not change them to bright glazes.

Glazes of this type containing 55 per cent or more flint show segregation and will not lie down to smooth surfaces from cones 12 to 16.

The proper way to correct crazing in this type of glaze is by increasing the alumina through the addition of clay. Higher fire causes the crazing area to recede, but not enough to make higher fire a safe way to correct crazing, except in the glazes containing 4 or less equivalents of silica. There seems to be evidence that this type of glaze will craze when overburned sufficiently, which might be worthy of further investigation.

Addition of flint to this type of glaze will not stop crazing, but if carried far enough may throw the composition of the glaze into the crazing area. This is in agreement with Stull, who found Seger's rule did not hold for this type of glaze.

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